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CHEMICAL CONVERSION OF NITROCELLULOSE FOR FERTILIZER



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20. Abstract (Cont'd)

3 hours. NC can also be degraded by hydrazine-hydrate. The only carbon product obtained was cellulose.

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Preface

The waste waters from nitrocellulose (NC) preparation contain a large amount of suspended "fines". The presence of these "fines" in waste streams is a potential pollution problem. The objective of the work described herein was to devise nonpolluting methods for the disposal of waste NC by chemical means.

Preface

The waste waters from nitrocellulose (NC) preparation contain a large amount of suspended "fines". The presence of these "fines" in waste streams is a potential pollution problem. The objective of the work described herein was to devise nonpolluting methods for the disposal of waste NC by chemical means.

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Chemical Conversion of Nitrocellulose for Fertilizer

Introduction: The waste waters from the final stages of nitrocellulose preparation contain a large amount of suspended NC "fines". It is these "fines" which constitute a pollution problem for industry. The amount of this material varies from 50 to 600 mg/l. Presently most of this NC is removed by centrifugation and/or filtration and then recycled. However, there are times when large amounts of NC of uncertain purity cannot be re-used and must be destroyed.

Several methods are used to dispose of this material. One method which is used in industry, is burning in open pits. This process consumes a large amount of energy and releases various amounts of nitrogen oxides to the atmosphere which are additional pollutants. Another method is the reaction of NC with water at elevated temperatures and pressures. Some of the products formed are CO_2 , N_2O , CO , HCN , NH_3 , and formic, tartaric, hydroxypyruvic, nitric, and nitrous acids.¹ Nitrocellulose can also be decomposed by strong alkali, and there are many references on the use of alkali such as sodium hydroxide for this decomposition.²⁻⁷ The use of

¹E. Knecht and B. R. Bostock, J. Soc. Chem. Ind. 39, 163T (1920).

²A. Bechamp, Compt. rend., 41, 817 (1855).

³H. Vohl, Dinglers Polytech. J., 112, 236 (1849).

⁴E. Bert and A. Fodor, Z. ges. Schiesso-uSprengstoff., 5, 296 (1910).

⁵O. Silberrad and R. C. Farmer, J. Chem. Soc., 89, 1759 (1906).

⁶I. M. Lowry, K. C. Browning and J. W. Farmery, J. Chem. Soc., 117, 552 (1920).

⁷E. M. Berland and W. Smith, Jr., J. Soc. Chem. Ind. 27, 534 (1908).

aqueous alkali does not result in simple cleavage of the nitrate ester groups to give cellulose and alkali nitrates, but instead leads to complete degradation of the cellulose polymer. The main products are various hydroxy and polycarboxylic acids and sodium nitrate and nitrite.

Objectives: The objective of the work summarized in this report was primarily to develop an economical and nonpolluting method of decomposing waste nitrocellulose, and secondly to determine whether a useful product, such as a fertilizer, could be obtained from this material.

Discussion: Part A. Nitrocellulose is a polymer of anhydroglucose units which have been nitrated. The extent of nitration for explosive grade NC is 2.6 moles of nitrogen per anhydroglucose unit. This corresponds to 12.5% nitrogen per anhydroglucose unit. Fully nitrated cellulose would have three nitro groups per anhydroglucose unit and analyse for 14.1% nitrogen. The nitrocellulose used in this research was obtained from Radford Army Ammunition Plant (RAAP), VA, and analysed for 12.5% nitrogen.

Since nitrocellulose contains 12% to 14% nitrogen it was suggested that this material might make a good fertilizer, if the nitrogen could be converted to a usable form.

From work done on the degrading of nitrocellulose with strong alkali, it had been shown that alkali nitrite was formed. If a weaker

base such as ammonium hydroxide were used for the degradation, then possibly the nitrate ester groups might form ammonium nitrate and nitrite, which are known to be good fertilizers.

Since little previous work had been done on the feasibility of decomposing NC with a weak base, such as NH_4OH , preliminary experiments were carried out to determine the effectiveness of this base. The extent of NC decomposition with NH_4OH at various concentrations and temperatures are shown in table 1.⁸ In all cases the concentration of NH_4OH shown is the concentration at room temperature. In those reactions carried out at temperatures of 75°C and above, the concentration of ammonia decreased as the temperature increased due to loss of ammonia from the open system. For example at 75°C it was found that the NH_4OH concentration was only 7%. After the initial loss of ammonia a new equilibrium was established at the higher temperature and the concentration of ammonia remained constant.

From table 1 it can be seen that in order to decompose NC in a reasonable length of time, elevated temperatures must be used.

The effect of varying the molar ratio of NH_4OH to NC is shown in table 2.⁸ NC is only 60% degraded using a fivefold excess of ammonia

⁸Some of the results shown in tables 1, 2, and 3 are summarized from Technical Report TR-75-14-FSL; Decomposition of NC Using Aqueous Ammonia; L. M. Dogliotti, R. C. Chalk, L. A. Spano, and D. H. Sieling, July 1974.

Table 1

% NC	% NH_4OH	Time (h)	Temp.	% Unreacted NC
5	10	16	R.T.	100
5	29	120	R.T.	3
5	10	164	50°C	7
5	10	1	98°C	50
5	10	4	75°C	5-7
5	10	8	75°C	0

Table 2

% NC	% NH_4OH	Molar* Ratio	% Unreacted NC
5	5	8.5/1	39
10	15	12.7/1	5
5	10	17/1	1-2
5	15	25.5/1	1-2

*Molar ratio of ammonium hydroxide to IIC.
All reactions were done at 75°C for 4 hours.

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5	10	104	50°C	7
5	10	1	98°C	50
5	10	4	75°C	5-7
5	10	8	75°C	0

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in 4 hours at 75°C. However when a tenfold excess is used, the NC is almost 100% degraded.

Table 3⁸ summarizes those experiments which were carried out at a constant molar ratio of ammonium hydroxide to NC and at a constant temperature. Under the experimental conditions used, after 4 hours only 60% of the NC had decomposed. By increasing the reaction time to 8 hours, practically all of the NC decomposed.

As previously noted, at elevated temperatures in an open system, some ammonia is lost. In order to avoid this loss and increase the efficiency of the degradation of NC, the use of a closed system was investigated.

Various molar ratios of ammonium hydroxide and NC were placed in a pressure vessel and sealed. The temperature was increased to 90°C. During the time of reaction the internal pressure was monitored. Periodically, gaseous samples were withdrawn for gas chromatographic analysis. The results obtained are shown in table 4. In less than 4 hours a 5% suspension of NC in 5% NH_4OH is completely decomposed in a closed system, whereas in an open system approximately 8 hours is required.

The decomposed solutions from NC are dark brown in color and when concentrated give a dark sticky residue. Since NC is practically insoluble in NH_4OH , and all other products formed are soluble, unreacted NC can be easily filtered out of the solution, and the amount of

Table 3

Molar Ratio*	Time (h)	% NC Unreacted
8.5/1	4	39
8.5/1	7	~ 2
8.5/1	8	~ 1
8.5/1	10	0

Reaction temp. = 75°C.

Table 4

% NC	% NH ₄ OH	Time (h)	Temp.	Press.	% Unreacted NC
5	1 (1.7/1)*	19	90°C	16 lbs./sq. in.	60
5	3 (5.1/1)*	4	90°C	20	9
5	5 (8.5/1)*	3	90°C	16	0

*Molar ratio of NH₄OH to NC.

unreacted HC determined. Infrared spectroscopy was used to identify this material as HC by its characteristic bands at 1225, 1275 and 1650 cm^{-1} . An infrared spectroscopic examination of the dark residue gave bands characteristic of ammonium nitrite and nitrate as well as salts of organic acids. Further evidence for the presence of ammonium nitrate and nitrite was obtained when these compounds sublimed during the concentration of the decomposed HC solutions.

The gas chromatographic analysis of the gases formed during the decomposition in a closed system showed only the presence of CO_2 , initially. As the reaction proceeded at an elevated temperature, N_2O began to appear as well. After 3 hours at 90°C the amounts of CO_2 and N_2O were about equal. After the reaction was completed, and the solution cooled down to room temperature, the major gaseous component was N_2O . This nitrous oxide probably arises from the breakdown of ammonium nitrate and nitrite at elevated temperatures.

The residue from a fully decomposed HC suspension contained from 18% to 22% N as shown by an elemental analysis. The theoretical value for N based on 2.6 equivalents of ammonia used for the 2.6 nitro groups per anhydroglucose unit would be 19%. This range of nitrogen values found results partly from the loss of some of the nitrogen as N_2O thus giving lower values. If the decomposition is carried out at lower temperatures, the amount of nitrous oxide formed is decreased and the percentage of nitrogen in the residue increases.

Also contributing to the nitrogen value is the formation of ammonium salts of carboxylic acids generated from the breakdown of the cellulose chain. In all cases of complete nitrocellulose decomposition, more than 3 equivalents of ammonium hydroxide were used due to the formation of these salts.

Discussion: Part B. Recently it was reported that the nitro groups of methyl 2,3-dinitroglucopyranoside could be selectively removed by hydrazine-hydrate, to give methyl glucopyranoside in nearly quantitative yields.⁹ The formation of a compound with the same configuration as the starting material indicates that the bond cleavage occurred between the oxygen atom attached to carbon and the nitrogen atom of the nitro group. If this same reaction could be applied to NC then the only carbon product obtained would be cellulose. The results from several experiments with hydrazine-hydrate and NC are shown in table 5.

When NC was dissolved in tetrahydrofuran and reacted with hydrazine-hydrate a nearly quantitative yield of cellulose was obtained. This material gave an IR spectrum identical to cellulose and could also be degraded by Trichoderma viride to glucose and cellobiose. However an elemental analysis showed that 1% to 2% N was present. An IR spectrum showed no adsorption at 825 cm^{-1} which is characteristic of NC. Therefore this nitrogen most likely does not arise from partially degraded NC. It is possible that some hydrazine may be involved with

⁹K. S. Ennor and J. Honeyman, J. Chem. Soc., 1958, 2586.

Table 5

Moles - NO ₂	Moles H ₄ N ₂ ·H ₂ O	Temp.	Time (h)	Solvent.	% Cellulose
0.006	0.034	90-95°C	6	H ₂ O	50 (PPT)
0.0045	0.017	50°C	20	THF	95-100
0.0045	0.034	50°C	3	THF	95-100
0.0045	0.051	50°C	3	THF	95-100

the cellulose through hydrogen bonding or by occlusion in the crystalline structure. Some support for this is given by the reaction of NC with hydrazine-hydrate in water. In this case only about 50% of the cellulose precipitates from the reaction. The rest of the cellulose is in some type of a soluble form. This solubilized form when initially concentrated to dryness contains approximately 30% N which is not from nitro groups. If this material is dialysed in water it becomes insoluble and the nitrogen content is reduced to 1% to 2% and the dialysate contains hydrazine. It is possible that the solubilization of cellulose is brought about through hydrogen bonding with hydrazine thereby preventing the cellulose from being in its regular crystalline form which is insoluble in water.

Economical Feasibility: NC can be more economically degraded on a chemical cost basis by ammonium hydroxide than by hydrazine-hydrate. Anhydrous ammonia is presently selling for \$130 per ton (9×10^2 kg). If the reaction is done in an open system at 75°C using a 17:1 molar ratio of ammonium hydroxide to NC, then 8.76×10^2 kg (0.97 tons) of ammonia would be needed to degrade 9×10^2 kg (1 ton) of NC. Thus, the cost per ton would be \$126. This cost could be reduced since some of the excess ammonia could be recovered. If a closed system is used, the cost per ton would be \$63. Again excess ammonia could be collected and re-used. The cost of energy for the two systems should be about the same, since both could be heated with steam. In case of NC and hydrazine-hydrate (\$1.33/453 g) in water the cost per ton is \$3,078.

The cost of degrading NC with hydrazine-hydrate is considerably higher. At present hydrazine-hydrate is selling at \$1.33/453 g, therefore the cost per 9×10^2 kg (ton) would be \$3,078.

Experimental: Part A. General procedure: A known amount of nitro-cellulose, which had been air-dried, was suspended in 50 ml of ammonium hydroxide of known concentration. The slurry was then placed in a 250-ml pressure bottle. The bottle was wrapped with heating tape and attached to a Parr pressure apparatus. The slurry was shaken intermittently. During the course of the reaction the internal pressure and temperature were monitored. The reaction was stopped at various timed intervals and analysed for NC using the three characteristic IR bands (825, 1275, and 1650 cm^{-1}).

At the completion of the reaction, the resulting dark brown solution was filtered and concentrated to a thick dark syrup and again analysed for NC by IR.

Decomposition of NC with 1% NH_4OH : 2.5 gm of NC was reacted with 1% NH_4OH solution according to the general procedure above. After 19 hours at 90°C , 60% of the NC was still undecomposed.

Decomposition of NC with 3% NH_4OH : 2.5 gm of NC was reacted with a 3% NH_4OH solution at 90°C for 4 hours using the general procedure outlined above. Under these conditions, 9% unreacted NC was found.

Decomposition of NC with 5% NH_4OH : 2.5 gm of NC was reacted with 5% NH_4OH solution at 90°C for 4 hours using the general procedure outlined above. During the decomposition the pressure slowly increased to 16 lb/sq. in. Two samples of the atmosphere above the reaction mixture were withdrawn: one at the beginning of the reaction and one at the end. These samples were analysed by gas chromatography using 1.8 m x 6.35 mm Porapak Q column at room temperature. The first sample gave only one peak which had the same retention time as CO_2 . The second sample had two peaks of approximately equal area. The first corresponded to CO_2 and the second to H_2O .

The dark brown solution was concentrated in vacuo at 50°C to a dark gummy material. During the concentration a small amount of white crystals sublimed onto the neck of the flask. These crystals were ammonium nitrate. No evidence of NC was found by IR: 100% decomposition. Elemental analysis: 18% N.

Experimental: Part B. Reaction of NC with 0.017 moles hydrazine-hydrate in tetrahydrofuran: a 500-mg sample of NC was dissolved in 50 ml of tetrahydrofuran (THF). One ml of 85% hydrazine-hydrate was added and the solution warmed to 50°C . As the reaction proceeded, the clear solution became cloudy and a white solid precipitated. Small aliquots of the solution were withdrawn periodically and analysed for NC using IR. After 20 hours no NC was detected and the reaction was stopped. The solid material was filtered off and washed with THF and H_2O . IR of

the solid was the same as the IR spectrum of cellulose. A nearly quantitative yield of cellulose was obtained.

Hydrazine-hydrate (0.034 moles) in THF: the reaction was carried out as above except 2 ml of hydrazine-hydrate was used. All of the NC had reacted in 3 hours.

Hydrazine-hydrate (0.05 moles) in THF: 3 ml of hydrazine-hydrate was used. No appreciable difference in the overall reaction was noted.

Reaction of NC with hydrazine-hydrate in water: NC (520 mg) was suspended in 50 ml of water. To this suspension was added 2 ml of 85% hydrazine-hydrate and the mixture heated to 90°C. When the reaction mixture became clear, approximately 6 hours, the reaction was stopped. On cooling, some material precipitated and was filtered off (90 mg). This material was shown by IR to be cellulose. The filtrate, which was basic, was concentrated in vacuo to 15 ml and then titrated with HCl to a pH of 5.5. During this time additional cellulose precipitated and was removed by filtration (54 mg). This filtrate was then dialysed overnight (18 hours). The dialysed material was concentrated to dryness giving 179 mg of a tan solid. An elemental nitrogen analysis showed 3% nitrogen present. No bands characteristic of NC were found in an IR spectrum of the solid. This solid was redissolved in a minimum of water. Ethanol was added causing a precipitate to form. The solid was removed by filtration, dried, and analysed. The nitrogen content was now 5% and the IR spectrum was the same as cellulose. Further dialysis of

this material gave a completely water insoluble solid which was cellulose. The overall yield of cellulose was approximately 85%.

Conclusion: A 5% suspension of NC can be degraded completely with 10% aqueous ammonia when heated to 75°C for 8 hours in an open system. If a closed system is used only 5% aqueous ammonia and 3 hours of heating is needed. The residue obtained in both cases contains from 18% to 22% nitrogen.

The nitro groups can be removed from NC without destroying the cellulose by using hydrazine-hydrate in water. The yield of cellulose is 95% to 100%.

Although hydrazine-hydrate degradation gives a cleaner residue than ammonia, the cost on a chemical basis is higher. To degrade 9×10^{-2} kg (1 ton) with hydrazine-hydrate would cost approximately \$3,000, whereas with ammonia it could be as low as \$60.

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